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(54) **Fire retardant polyester resin composition and process for producing the same**

(57) A fire retardant polyester resin composition comprising (A) 95 to 30 parts by weight of a polyester resin and (B) 5.0 to 70 parts by weight of a polyphenylene ether resin and/or polyphenylene sulfide resin, and, for 100 parts by weight in total of the components (A) and (B), (C) 0.05 to 10 parts by weight of a compatibilizing agent, (D) 2.0 to 45 parts by weight of a phosphoric ester compound or phosponitrile compound, (E) 0 to 150 parts by weight of a reinforcing filler, (F) 0.001

to 15 parts by weight of an anti-dripping agent, (G) 0 to 45 parts by weight of a melamine cyanurate, and (H) 0 to 15 parts by weight of a polystyrene resin having epoxy group, provided that the amount of the component (G) is from 0.5 to 45 parts by weight for 100 parts by weight in total of the components (A) and (B) when the amount of the component (B) is less than 35 parts by weight. The polyester resin composition scarcely corrodes a metal mold when it is molded, and is excellent in fire retardancy.

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Description**BACKGROUND OF THE INVENTION****Field of the Invention**

The present invention relates to a fire retardant polyester resin composition. More particularly, the present invention relates to a fire retardant polyester resin composition having excellent mechanical properties, flow characteristics, resistance to hydrolysis and dimensional stability as well as high fire retardancy.

Background Art

In recent years, thermoplastic polyester resins are widely used for injection-molded products such as automotive parts, electrical parts and electronic parts. Materials for use in these applications are now required to have not only excellent mechanical properties and molding properties but also high fire retardancy. Heretofore, organic fire retardants such as bromine- or chlorine-containing ones have been extensively used for polyester resins. However, these fire retardants are disadvantageous in that they evolve a large amount of hydrogen bromide or hydrogen chloride gas, which is poisonous and corrosive, and black smoke while they are burning.

Water-containing inorganic compounds such as magnesium hydroxide and aluminum hydroxide have been known as non-bromine or non-chlorine fire retardants. However, the fire-retardancy-imparting properties of these water-containing inorganic compounds are not so excellent as those of bromine or chlorine fire retardants. Therefore, in order to obtain a product having high fire retardancy by the use of such an inorganic compound, it is necessary to incorporate a large amount of the inorganic compound into a resin. If a large amount of the inorganic compound is incorporated into a resin, the resin considerably deteriorates in mechanical properties and molding properties.

Further, there has been known a method in which a nitrogen compound having triazine ring is incorporated into a resin as a fire retardant (Japanese Patent Publications Nos. 5939/1983 and 33850/1985). However, such a nitrogen compound is poor in fire-retardancy-imparting properties, and also has some other shortcomings; for instance, the nitrogen compound incorporated into a resin considerably deteriorates the resulting molded product in mechanical properties, stains the metal mold used, and bleeds at the surface of the resin. Furthermore, a variety of phosphorus compounds have also been known as non-bromine or non-chlorine fire retardants.

Red phosphorus is excellent in fire-retardancy-imparting properties. Therefore, even when a relatively small amount of red phosphorus is incorporated into a polyester resin, the resin can show high fire retardancy. However, the red phosphorus incorporated into the resin makes the final product reddish, and also considerably deteriorates the polyester resin in mechanical properties when the temperature and humidity are high. Red phosphorus is thus unsatisfactory from the practical point of view.

There has also been known a method in which a phosphoric ester fire retardant is incorporated into a resin (Japanese Patent Publications Nos. 19858/1976 and 39271/1976). However, fire retardants of this type are poor in fire-retardancy-imparting properties as compared with bromine or chlorine fire retardants. Therefore, in order to impart high fire retardancy to a resin by using such a phosphoric ester fire retardant, it is necessary to incorporate a large amount of this fire retardant into the resin. When a large amount of a phosphoric ester fire retardant is incorporated into a resin, the crystallinity of the resin is greatly lowered. The resin therefore undergoes remarkable deterioration in mechanical properties and molding properties. Moreover, the phosphoric ester fire retardant extremely lowers the resistance to hydrolysis of the polyester resin. In addition, the phosphoric ester fire retardant incorporated into the resin in a large amount in order to impart high fire retardancy to the resin not only severely causes plate-out when the resin is molded, but also bleeds at the surface of the final product. This makes the appearance of the final product poor, and brings about contact failure.

Japanese Laid-Open Patent Publication No. 47056/1985 discloses a fire retardant polyester resin composition which is obtained by adding a polyphenylene ether resin and a bromine or chlorine fire retardant to a thermoplastic linear polyester resin and an organic phosphoric ester so as to supplement the insufficient fire-retardancy-imparting properties of the phosphoric ester fire retardant. However, this composition has a drawback in that it evolves irritating gases and a large amount of black smoke while it is burning due to the bromine or chlorine fire retardant contained in the composition.

Furthermore, Japanese Laid-Open Patent Publication No. 339493/1993 discloses a fire retardant polyester resin composition comprising a saturated polyester resin, a polyphenylene ether resin and red phosphorus. Red phosphorus is poor in thermal stability, and makes the final product reddish, so that this composition is also still unsatisfactory from the practical point of view.

SUMMARY OF THE INVENTION

The present invention is intended to solve the aforementioned problems in the prior art.

An object of the present invention is therefore to provide a fire retardant polyester resin composition which comprises a fire retardant containing no bromine or chlorine atom, which evolves no corrosive gases when it is molded, which scarcely evolves irritating and corrosive gases and black smoke while it is burning and which has excellent mechanical properties, flow characteristics, resistance to hydrolysis, molding properties and dimensional stability as well as high fire retardancy.

We made earnest studies in order to attain the above object of the invention, and, as a result, found that a polyester resin composition comprising specific components having specific structures is excellent in fire retardant properties, mechanical properties, flow characteristics, resistance to hydrolysis and dimensional stability. The present invention has been accomplished on the basis of this finding.

Thus, the present invention provides a fire retardant polyester resin composition comprising the following components (A) to (H) :

- (A) 95 to 30 parts by weight of a polyester resin, and
 - (B) 5.0 to 70 parts by weight of a polyphenylene ether resin and/or polyphenylene sulfide resin, and, for 100 parts by weight in total of the components (A) and (B),
 - (C) 0.05 to 10 parts by weight of a compatibilizing agent,
 - (D) 2.0 to 45 parts by weight of a phosphoric ester compound or phosphonitrile compound,
 - (E) 0 to 150 parts by weight of a reinforcing filler,
 - (F) 0.001 to 15 parts by weight of an anti-dripping agent,
 - (G) 0 to 45 parts by weight of a melamine cyanurate, and
 - (H) 0 to 15 parts by weight of a polystyrene resin having epoxy group,
- provided that the amount of the component (G) is from 0.5 to 45 parts by weight for 100 parts by weight in total of the components (A) and (B) when the amount of the component (B) is less than 35 parts by weight.

The present invention also provides a process for producing a fire retardant polyester resin composition comprising the following components (A) to (H):

- (A) 95 to 30 parts by weight of a polyester resin, and
 - (B) 5.0 to 70 parts by weight of a polyphenylene ether resin and/or polyphenylene sulfide resin, and, for 100 parts by weight in total of the components (A) and (B),
 - (C) 0.05 to 10 parts by weight of a compatibilizing agent,
 - (D) 2.0 to 45 parts by weight of a phosphoric ester compound or phosphonitrile compound,
 - (E) 0 to 150 parts by weight of a reinforcing filler,
 - (F) 0.001 to 15 parts by weight of an anti-dripping agent,
 - (G) 0 to 45 parts by weight of a melamine cyanurate, and
 - (H) 0 to 15 parts by weight of a polystyrene resin having epoxy group,
- provided that the amount of the component (G) is from 0.5 to 45 parts by weight for 100 parts by weight in total of the components (A) and (B) when the amount of the component (B) is less than 35 parts by weight, in which the polyester resin (the component (A)), the polyphenylene ether resin and/or polyphenylene sulfide resin (the component (B)) and the compatibilizing agent (the component (C)) are firstly melt-kneaded to form a mixture, and the mixture is then melt-kneaded with the other components (D) to (H) to obtain the desired fire retardant polyester resin composition.

The polyester resin composition of the present invention is excellent in fire retardancy. In addition, the composition contains no bromine or chlorine compound as a fire retardant, so that it scarcely evolves corrosive gases during the step of molding. Further, the composition is also excellent in mechanical properties, resistance to hydrolysis, flow characteristics and dimensional stability, and produces neither volatile products nor decomposition products when it is molded or used for a long period of time. Therefore, the polyester resin composition of the present invention can be suitably used for producing electrical parts and electronic parts.

DETAILED DESCRIPTION OF THE INVENTION

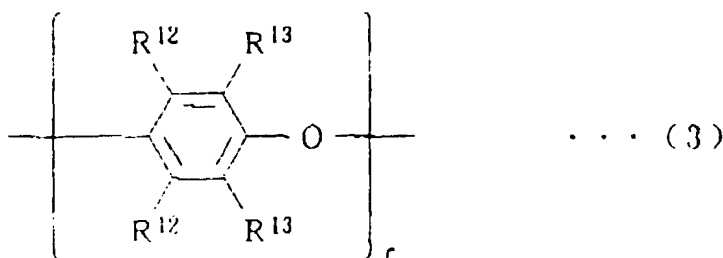
The polyester resin, the component (A), used for producing the fire retardant polyester resin composition of the invention is a thermoplastic polyester having an intrinsic viscosity of 0.50 or higher, obtained by the condensation polymerization of at least one bifunctional carboxylic acid component and at least one glycol component or hydroxy-

carboxylic acid. Specific examples of the bifunctional carboxylic acid component include terephthalic acid, isophthalic acid, 2,6-naphthalene-dicarboxylic acid, 2,7-naphthalenedicarboxylic acid, p,p-di-phenyldicarboxylic acid, p,p-diphenyl ether carboxylic acid, adipic acid, sebacic acid, dodecandioic acid, suberic acid, azelaic acid, and 5-sodium sulfoisophthalic acid, and ester-forming derivatives thereof. Of these, aromatic dicarboxylic acids and ester-forming derivatives thereof are preferred, and terephthalic acid and terephthalic diesters are particularly preferred.

Specific examples of the glycol component include those compounds which are represented by the general formula $\text{HO}(\text{CH}_2)_q\text{OH}$ wherein q is an integer of 2 to 20, such as alpha, omega-alkylene glycols, neopentyl glycol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, bisphenol A, polyoxy-ethylene glycol and polyoxytetramethylene glycol, and ester-forming derivatives thereof. Of these, alpha, omega-alkylene glycols such as ethylene glycol and 1,4-butanediol are preferred, and 1,4-butanediol is particularly preferred.

Specific examples of the hydroxycarboxylic acid include hydroxybenzoic acid and 4-(2-hydroxyethoxy)benzoic acid, and ester-forming derivatives thereof. When 70 mol% or more of all of the acid or diol components which are used for producing the polyester is a single component, any copolymer may also be used. Further, a mixture of 60% by weight or more of the polyester resin and 40% by weight or less of other thermoplastic polymer such as polycarbonate or ABS resin can also be used in the present invention.

In the polyphenylene ether resin (hereinafter referred to as "PPE") and/or polyphenylene sulfide resin (hereinafter referred to as "PPS"), the component (B), used for producing the fire retardant polyester resin composition of the present invention, the PPE is a homopolymer or copolymer having the structure represented by the following general formula (3):

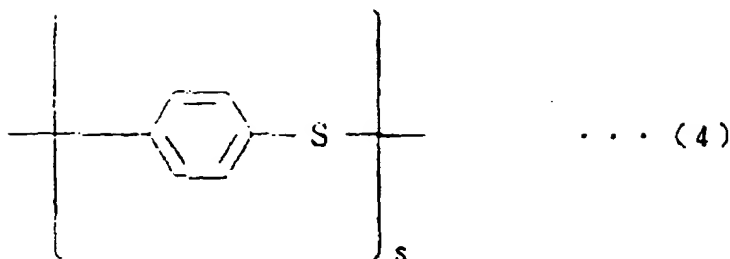


wherein R^{12} represents hydrogen atom, a primary or secondary alkyl group, an aryl group, an aminoalkyl group or a hydrocarbon hydroxy group, R^{13} represents a primary or secondary alkyl group, an aryl group or an aminoalkyl group, and r is an integer of 10 or more.

The primary alkyl group represented by R^{12} or R^{13} is methyl, ethyl, n-propyl, n-butyl, n-amyl, isoamyl, 2-methylbutyl, n-hexyl, 2,3-dimethylbutyl, 2,3- or 4-methylpentyl, or heptyl. Preferable examples of the secondary alkyl group represented by R^{12} or R^{13} include isopropyl, sec-butyl or 1-ethylpropyl. A suitable PPE homopolymer is, for instance, a polymer consisting of 2,6-dimethyl-1,4-phenylene ether unit. A suitable PPE copolymer is a random copolymer consisting of the above unit and 2,3,6-trimethyl-1,4-phenylene ether unit in combination.

The intrinsic viscosity of the PPE, the component (B), for use in the present invention, determined at 30°C in chloroform is preferably 0.2 to 0.8 dl/g, more preferably 0.25 to 0.7 dl/g, particularly 0.3 to 0.6 dl/g. When a PPE having an intrinsic viscosity of less than 0.2 dl/g is used, the resulting composition is insufficient in impact resistance. On the other hand, a PPE having an intrinsic viscosity of more than 0.8 dl/g has a high gel content. Therefore, when such a PPE is used, the resulting molded product has a poor appearance.

A PPS can also be used as the component (B), and it is particularly preferable to use a PPS along with the PPE. The PPS for use in the present invention is a homopolymer or copolymer having the structure represented by the following general formula (4):



wherein s is an integer of 10 or more. The PPS homopolymer or copolymer contains the above repeating unit in an amount of 70 mol% or more, preferably 90 mol% or more, most preferably almost 100 mol%. The PPS copolymer may comprise, as the component copolymerized, metha, ether, sulfone or biphenyl linkage, amino-, carboxyl-, alkyl-, nitro-, phenyl- or alkoxy-substituted phenylsulfide linkage or trifunctional phenylsulfide linkage as long as the amount of such a component is less than 30 mol%. The amount of the copolymerised component in the PPS copolymer is preferably less than 10 mol%, particularly less than 5 mol%.

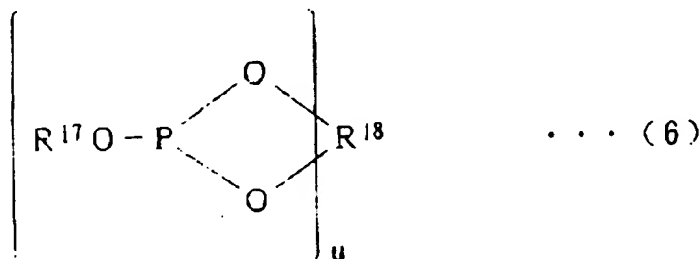
In the case where the PPE and the PPS are used in combination, the weight ratio of the PPE to the PPS is 99:1 to 5:95, preferably 90:10 to 20:80, most preferably 70:30 to 30:70. When the proportion of the PPE is decreased to less than 5, the composition deteriorates in mechanical properties.

The component (B), the PPE and/or the PPS, is used in such an amount that the weight ratio of the component (A), the polyester resin, to the component (B) will be 95:5 to 30:70, preferably 90:10 to 40:60, particularly 80:20 to 60:40. When the proportion of the component (B) is less than 5, the resulting composition is insufficient in fire retardancy and resistance to hydrolysis. On the other hand, when the proportion of the component (B) is increased to more than 70, the composition considerably deteriorates in flow characteristics and molding properties.

The compatibilizing agent, the component (C), used for producing the fire retardant polyester resin composition of the present invention is a compound which can improve the dispersion properties of the PPE and/or the PPS in the polyester resin. It is possible to use, as such a compound, a polycarbonate resin, a compound having one or more carboxyl, carbonic ester, acid amide, imide, acid anhydride, epoxy, oxazolinyl, amino or hydroxyl groups, or a phosphorous ester compound. Specific examples of the compatibilizing agent include an epoxy-group-added PPE resin, a hydroxyalkylated PPE resin, a PPE resin having an oxazolinated end, polyester whose carboxyl end group is modified with polystyrene, polyester whose OH end group is modified with polyethylene, and phosphorous esters. Of these, phosphorous esters are preferred, and phosphorous triesters are more preferred from the viewpoints of the resistance to hydrolysis, crystallinity, mechanical properties and fire retardancy of the composition. In particular, phosphorous triesters which can be suitably used in the present invention are those ones which are represented by the following general formula (5):

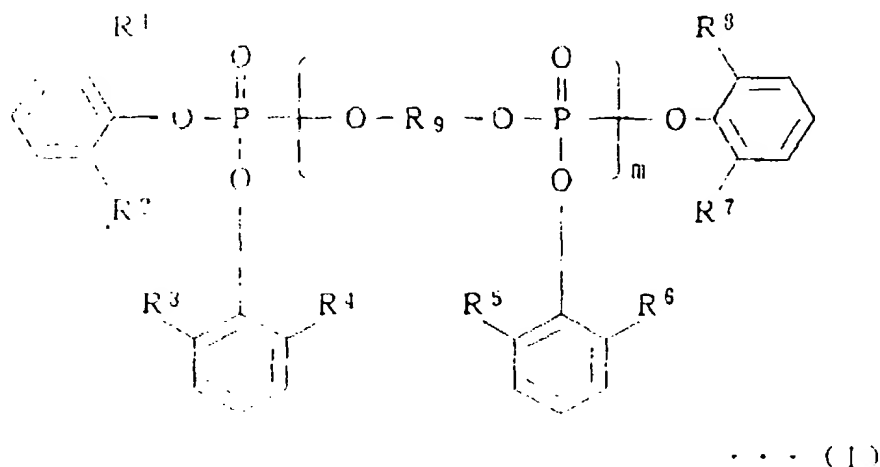


wherein R^{14} , R^{15} and R^{16} represent an alkyl group having 1 to 20 carbon atoms, or a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, and may contain oxygen, nitrogen or sulfur atom; or the following general formula (6):

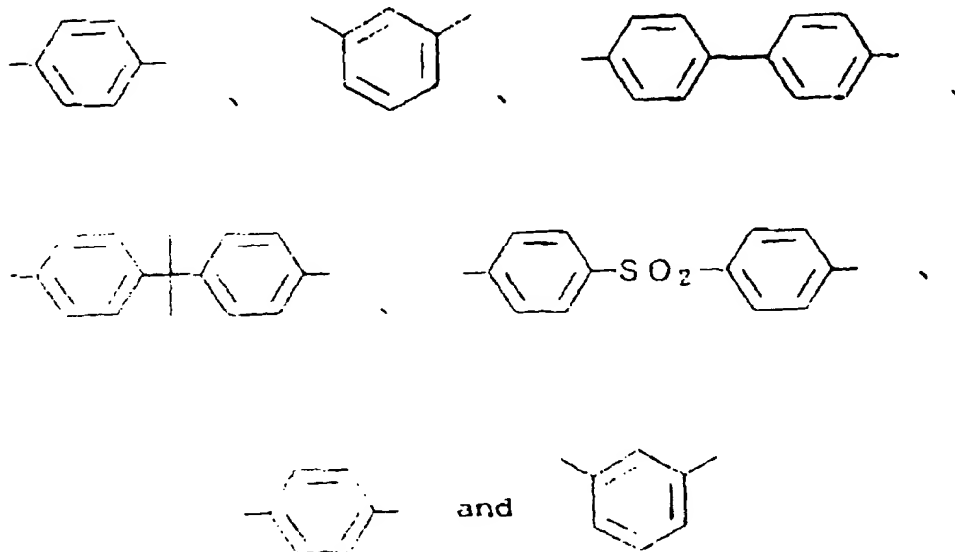


parts by weight of the component (C) is used, the resulting composition has lowered fire retardancy, and the final product has a poor appearance.

Specific examples of the phosphoric ester compound, the component (D), used for producing the fire retardant polyester resin composition of the present invention include trimethyl phosphate, triethyl phosphate, tributyl phosphate, trioctyl phosphate, tributoxyethyl phosphate, triphenyl phosphate, tricresyl phosphate, cresyldiphenyl phosphate and octyldiphenyl phosphate. Of these, those compounds which are represented by the following general formula (1) are preferred:



In the above formula (1), R¹ to R⁸ represent hydrogen atom, or an alkyl group having 1 to 6 carbon atoms. In order to impart improved resistance to hydrolysis to the composition, it is preferable that R¹ to R⁸ be an alkyl group having not more than 6 carbon atoms, more preferably an alkyl group having not more than 2 carbon atoms, especially methyl group. m is 0 or an integer of 1 to 4, preferably an integer of 1 to 3, especially 1. R⁹ represents a structure selected from the following:

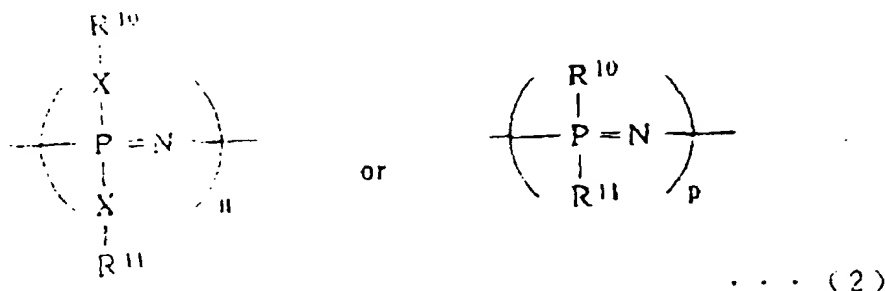


are preferred, and



is particularly preferred.

A phosphonitrile compound having a group represented by the following general formula (2) can also be suitably used as the component (D):



wherein X represents O, S, or N-H; R^{10} and R^{11} are an aryl, alkyl or cycloalkyl group having 1 to 20 carbon atoms, -X- R^{10} and -X- R^{11} may be same or different, and n and p are an integer of 1 to 12.

In the above formula (2), R^{10} and R^{11} are an aryl, alkyl or cycloalkyl group having 1 to 20 carbon atoms. Specific examples of these groups include methyl, ethyl, butyl, hexyl, cyclohexyl, phenyl, benzyl and naphthyl. n and p are an integer of 1 to 12; they are usually an integer of 3 to 10, and an integer of 3 or 4 is particularly preferred. The phosphonitrile compound may be either a linear polymer or a cyclic polymer, and a cyclic polymer is suitably used in the present invention. In the above formula (2), X represents O, S, or N-H. Of these, O and N-H are preferred, and O is particularly preferred.

The component (D) is used in an amount of 2.0 to 45 parts by weight, preferably 3.0 to 40 parts by weight, particularly 5.0 to 30 parts by weight for 100 parts by weight in total the components (A) and (B). When less than 2.0 parts by weight of the component (D) is used, the resulting composition is insufficient in fire retardancy. When the amount of the component (D) is increased to more than 45 parts by weight, the composition considerably deteriorates in mechanical properties, resistance to hydrolysis and molding properties.

The reinforcing filler, the component (E), used for producing the fire retardant polyester resin composition of the present invention may be either an organic compound or an inorganic compound. Examples of the reinforcing filler include glass fiber, glass flake, glass bead, milled fiber, alumina fiber, silicon carbide fiber, boron fiber, carbon fiber, aramid fiber, and whiskers of alumina, silicon oxide, magnesium oxide, aluminum oxide, zirconium oxide, titanium oxide, carbonates such as calcium carbonate, magnesium carbonate and dolomite, calcium sulfate, barium sulfate, zirconium phosphate, boron nitride, silicon carbide and potassium titanate. The mean aspect ratio of the reinforcing filler, the component (E), after it is incorporated into the polyester resin composition is preferably 3.0 or more, more preferably 5.0 or more, most preferably 10 or more.

The above-enumerated materials are used either singly or in combination of two or more as the reinforcing filler, the component (E). In general, it is preferable to treat, in advance, the materials with a silane or titanium coupling agent, or the like. Further, in order to increase the adhesion between the coupling agent and the polyester resin composition, an acid anhydride such as maleic anhydride may be added, and, at the same time, an organic peroxide may also be added to further increase the adhesion. The reinforcing filler, the component (E), is used in an amount of 0 to 150 parts by weight, preferably 10 to 140 parts by weight, more preferably 20 to 130 parts by weight for 100 parts by weight in total of the components (A) and (B). When the amount of the component (E) is increased to more than 150 parts by weight, the composition considerably deteriorates in flow characteristics.

The anti-dripping agent, the component (F), used for producing the polyester resin composition of the present invention is a compound having the properties of preventing a resin from dripping the resin is burning. Specific examples of the anti-dripping agent include silicone oils, silica, asbestos, fluorine-containing polymers, and layered silicates such as talc and mica. Of these, fluorine-containing polymers, silicone oils and layered silicates are preferable as the anti-

dripping agent when the fire retardancy of the composition is taken into consideration.

Examples of the fluorine-containing polymers include fluorinated polyolefins such as polytetrafluoroethylene, tetrafluoroethylene/perfluoroalkylvinyl ether copolymers, tetrafluoroethylene/hexafluoropropylene copolymers, tetrafluoroethylene/ethylene copolymers, vinylidene fluoride and polychlorotrifluoroethylene. Of these, polytetrafluoroethylene, tetrafluoroethylene/perfluoroalkylvinyl ether copolymers, tetrafluoroethylene/hexafluoropropylene copolymers and tetrafluoroethylene/ethylene copolymers are more preferred, and polytetrafluoroethylene and tetrafluoroethylene/hexafluoropropylene copolymers are particularly preferred.

Further, the melt viscosity at 350°C of the fluorine-containing polymer for use in the present invention is preferably 1.0×10^3 to 1.0×10^{16} poises, more preferably 1.0×10^4 to 1.0×10^{15} poises, particularly 1.0×10^{11} to 1.0×10^{13} poises. When a fluorine-containing polymer having a melt viscosity of lower than 1.0×10^3 poises is used, there is a tendency that the resulting composition cannot show sufficiently high resistance to dripping while it is burning. On the other hand, when a fluorine-containing polymer having a melt viscosity of higher than 1.0×10^{16} poises is used, the resulting composition tends to be poor in flow characteristics.

The silicone oil used as the component (F) is a compound having dimethyl polysiloxane skeleton represented by the following general formula (8):



wherein t is an integer of 3 or more. A part of or all of the terminal ends or side chains of such a compound may be substituted with functional groups by undergoing amino-, epoxy-, carboxyl-, carbinol-, methacryl-, mercapto-, phenol-, polyether-, methylstyryl-, alkyl-, higher-fatty-ester-, higher-alkoxy- or fluoro-modification.

The viscosity at 25°C of the silicone oil for use in the present invention is preferably 1,000 to 30,000 cst, more preferably 2,000 to 25,000 cst, particularly 3,000 to 20,000 cst. When a silicone oil having a viscosity of lower than 1,000 cst is used, the resulting composition cannot show sufficiently high resistance to dripping while it is burning, and thus tends to have lowered fire retardancy. On the other hand, when a silicone oil having a viscosity of higher than 30,000 cst is used, the resulting composition has an increased viscosity, and thus tends to be poor in flow characteristics.

It is more preferable to use a layered silicate as the anti-dripping agent, the component (F), in the fire retardant polyester resin composition of the present invention from the viewpoint of the melt-flow characteristics of the composition. Examples of the layered silicates include layered silicates, modified layered silicates (layered silicates containing quaternary organic onium cation charged between their layers), and layered silicates or modified layered silicates additioned with a reactive functional group. Of these, modified layered silicate, and layered silicates or modified layered silicates additioned with a reactive functional group are preferred when the dispersion properties of the layered silicates in the polyester resin composition and the anti-dripping properties are taken into consideration. In particular, layered silicates or modified layered silicates additioned with a reactive functional group such as epoxy, amino, oxazoline, carboxyl or acid anhydride group can be suitably used in the present invention. There is no particular limitation on the method for preparing the layered silicates or modified layered silicates additioned with such a reactive functional group. However, a method in which a functionality-imparting agent (silane coupling agent) is used to treat a layered silicate or modified layered silicate is simple and preferred.

Specific examples of the silane coupling agent include chlorosilanes having epoxy group such as 3-glycidyloxypropyl-dimethylchlorosilane, beta-(3,4-epoxycyclohexyl)ethyl-dimethyl-chlorosilane and 3-glycidyloxypropyltrichlorosilane, chlorosilanes having carboxyl group such as trichlorosilyl-acetic acid, 3-trichlorosilylpropionic acid and 5-carboxyhexyl-dimethylchlorosilane, chlorosilanes having mercapto group such as 3-mercaptopropyl-dimethyltrichlorosilane, 3-mercaptopropyl-trichlorosilane and 4-mercaptophenyl-dimethylchlorosilane, alkoxysilanes having amino group such as 3-aminopropyltri-ethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane and N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, and alkoxysilanes having epoxy group such as 3-glycidyloxypropyl-methyldiethoxysilane, 3-glycidyloxypropyl-trimethoxysilane and beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane. Of these, chlorosilanes having epoxy group such as 3-glycidyloxypropyl-dimethylchlorosilane, beta-(3,4-epoxycyclohexyl)ethyl-dimethyl-chlorosilane and 3-glycidyloxypropyltrichlorosilane, alkoxysilanes having amino group such as 3-aminopropyltri-ethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane and N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, and alkoxysilanes having epoxy group such as 3-glycidyloxypropylmethyldiethoxysilane, 3-glycidyloxypropyltrimethoxysilane and beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane are preferred, and chlorosilanes having epoxy group

such as 3-glycidyloxypropyldimethylchlorosilane, beta-(3,4-epoxycyclohexyl)ethyl-dimethylchlorosilane and 3-glycidyloxypropyltrichlorosilane and alkoxysilanes having epoxy group such as 3-glycidyloxy-propylmethyldiethoxysilane, 3-glycidyloxypropyltrimethoxysilane and beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane are more preferred. In particular, alkoxysilanes having epoxy group such as 3-glycidyloxypropylmethyldiethoxysilane, 3-glycidyloxypropyltrimethoxysilane and beta-(3,4-epoxycyclohexyl)ethyl-trimethoxysilane are suitably used in the present invention. There is no particular limitation on the method for bringing the functionality-imparting agent into contact with a layered silicate. It is however preferable to attain this contact by mixing the functionality-imparting agent with the layered silicate without using a solvent or in a polar solvent.

Specific examples of the layered silicates which can be used in the present invention include smectite clay minerals such as montmorillonite, hectorite, fluorine hectorite, saponite, beidellite and subtincite, swelling synthetic micas such as Li-type fluorine taeniolite, Na-type fluorine taeniolite, Na-type tetrasilicon fluorine mica and Li-type tetrasilicon fluorine mica, vermiculite, fluorine vermiculite and halloysite. Thus, the layered silicates may be either natural or synthetic ones.

Of these, smectite clay minerals such as montmorillonite and hectorite, and swelling synthetic micas such as Li-type fluorine taeniolite, Na-type fluorine taeniolite and Na-type tetrasilicon fluorine mica are preferred, and montmorillonite and Na-type fluorine taeniolite are particularly preferred. These layered silicates can be used singly or in combination.

There is no particular limitation on the quaternary onium cation which is charged between the layers of the modified layered silicate for use in the present invention. Specific examples of the quaternary onium cation which can be suitably used include trimethylalkyl ammoniums such as trimethyloctyl ammonium, trimethyldecyl ammonium, trimethyldodecyl ammonium, trimethyltetradecyl ammonium, trimethylhexadecyl ammonium and trimethyloctadecyl ammonium, and dimethyldialkyl ammoniums such as dimethyldioctyl ammonium, dimethyldidecyl ammonium, dimethyldidodecyl ammonium, dimethylditetradecyl ammonium, dimethyldihexadecyl ammonium and dimethyldioctadecyl ammonium.

The amount of the anti-dripping agent, the component (F), in the polyester resin composition of the invention is from 0.001 to 15 parts by weight for 100 parts by weight in total of the components (A) and (B). When the component (F) is used in an amount of less than 0.001 parts by weight, the resulting composition is insufficient in anti-dripping properties. When the amount of the component (F) is increased to more than 15 parts by weight, the composition drastically deteriorates in flow characteristics and mechanical properties.

In the case where the above-described fluorine-containing polymer or silicone oil is used as the anti-dripping agent, the component (F), the amount of such a material is generally 0.001 to 10 parts by weight, preferably 0.005 to 8 parts by weight, particularly 0.01 to 5.0 parts by weight for 100 parts by weight in total of the components (A) and (B). When the above-described layered silicate is used as the anti-dripping agent, the component (F), the amount of such a material is generally 0.1 to 15 parts by weight, preferred 0.3 to 12 parts by weight, particularly 0.5 to 10 parts by weight for 100 parts by weight in total of the components (A) and (B).

The melamine cyanurate, the component (G), used for producing the polyester resin composition of the present invention is a product of an equimolar reaction between cyanuric acid and melamine. For instance, the melamine cyanurate can be obtained by mixing an aqueous solution of cyanuric acid with an aqueous solution of melamine, agitating the mixture at 90 to 100°C to allow the cyanuric acid and the melamine to react with each other, and separating the precipitate produced by means of filtration. The particle size of the melamine cyanurate is from 0.01 to 1,000 micrometers, preferably from 0.1 to 500 micrometers. Some of the amino or hydroxyl groups in the melamine cyanurate may be substituted with other substituents. The melamine cyanurate is used in an amount of 0 to 45 parts by weight, preferably 3.0 to 40 parts by weight, particularly 5.0 to 30 parts by weight for 100 parts by weight in total of the components (A) and (B). In particular, when the amount of the component (B) is less than 35 parts by weight, the melamine cyanurate is used in an amount of 0.5 to 45 parts by weight. When the melamine cyanurate is used in an amount of less than 0.5 parts by weight, the resulting composition cannot have sufficiently high fire retardancy. On the other hand, when the melamine cyanurate is used in an amount of more than 45 parts by weight, the resulting composition is poor in toughness and ductility, and also suffers from the bleed-out or plate-out of the melamine cyanurate.

There is no particular limitation on the ratio of the component (D) to the component (G), the melamine cyanurate. However, this ratio is generally 1.0:9.0 to 9.0:1.0, preferably 1.5:5 to 8.5:1.5, particularly 2.0:8.0 to 8.0:2.0.

On the other hand, when more than 35 parts by weight of the component (B) is used, it is not necessary to incorporate the melamine cyanurate so as to impart high fire retardancy to the polyester resin composition.

Examples of the polystyrene resin having epoxy group, the component (H), for use in the polyester resin composition of the invention include polymer compounds obtained by block- or graft-copolymerizing styrene and a polymer which is obtained by polymerizing a copolymerizable unsaturated monomer having epoxy group such as glycidyl methacrylate or acrylate, vinylglycidyl or allylglycidyl ether, glycidyl ether of hydroxyalkyl (meth)acrylate or of polyalkylene glycol (meth)acrylate, or glycidyl itaconate, comb-shaped polystyrene additioned with epoxy group, and polystyrene additioned with epoxy group.

There is no particular limitation on the structure of the polystyrene resin having epoxy group, and specific examples

of such a polystyrene resin include the following compounds: a comb-shaped polymer compound containing, as its main chain, a polymer obtained by polymerizing a copolymerizable unsaturated monomer having epoxy group, and, as its side chain, polystyrene; a straight-chain polymer compound obtained by block-copolymerizing polystyrene and a polymer which is obtained by polymerizing a copolymerizable unsaturated monomer having epoxy group; a comb-shaped polymer compound containing polystyrene as its main chain, and, as its side chain, a polymer which is obtained by polymerizing a copolymerizable unsaturated monomer having epoxy group; a comb-shaped polymer compound containing, as its main chain, polystyrene having epoxy group, and, as its side chain, polystyrene; and polystyrene additioned with a small number of epoxy groups. Of these, a comb-shaped polymer compound containing, as its main chain, a polymer obtained by polymerizing a copolymerizable unsaturated monomer having epoxy group, and as its side chain, polystyrene; a comb-shaped polymer compound containing, as its main chain, polystyrene having epoxy group, and, as its side chain, polystyrene; and modified polystyrene additioned with a small number of epoxy groups are preferred. A comb-shaped polymer compound containing, as its main chain, a polymer obtained by polymerizing a copolymerizable unsaturated monomer having epoxy group, and, as its side chain, polystyrene is particularly preferred. These polystyrene resins having epoxy group can be used either singly or as a mixture of two or more.

The weight-average molecular weight of the polystyrene in the polystyrene resin having epoxy group, the component (H) is generally 3,000 to 500,000, preferably 5,000 to 300,000, more preferably 20,000 to 200,000. When the weight-average molecular weight of the polystyrene is made to less than 3,000 or more than 500,000, the composition tends to deteriorate in impact resistance and flow characteristics. The polystyrene resin having epoxy group, the component (H), is used in an amount of 0 to 15 parts by weight, preferably not more than 12 parts by weight, particularly not more than 10 parts by weight for 100 parts by weight in total of the components (A) and (B). It is unfavorable to use more than 15 parts by weight of the polystyrene resin having epoxy group because the resulting composition may have extremely lowered fire retardancy.

The fire retardant polyester resin composition of the present invention can be obtained by mixing the above-described components, for instance, by a dry blending method in which the components are mixed by using a blender or mixer, or by a melt kneading method in which the components are melt-kneaded by using an extruder. A suitable method is such that, after the components are melt-kneaded and extruded into strand by a screw extruder, the strand is made into pellet. In this case, a method in which the three components of the polyester resin (component (A)), the PPE and/or PPS (component (B)) and the compatibilizing agent (component (C)) are firstly melt-kneaded to form a mixture, and the mixture is then mixed with the other components (D) to (H) to obtain the desired polyester resin composition is more preferable than a method in which all of the components (A) to (H) are melt-kneaded at the same time from the viewpoint of the flexural properties (flexural modulus and flexural strength) of the resulting composition. It is particularly preferable to add, when the components (A), (B) and (C) are mixed, a solvent in which the component (B) can be dissolved. Examples of such a solvent include xylene, toluene, trichlorobenzene, chloroform and α -chloronaphtalene. Of these, xylene and toluene are preferred, and xylene is particularly preferred from the viewpoints of the prevention of emission of corrosive gases and of the easiness of desolvation. The fire retardant polyester resin composition of the present invention can comprise other conventional additives such as light stabilizers, ultraviolet absorbers, antioxidants, antistatic agents, adhesion accelerators, crystallization accelerators, lubricants, coloring agents, foaming agents, plasticizers, thickening agents, drip-proofing agents, releasing agents, impact-resistance-improving agents and anti-smoking agents. The polyester resin composition can be molded by various molding methods such as injection, extrusion or compression molding method. Further, in order to improve the flow characteristics of the fire retardant polyester resin composition of the present invention, a polystyrene resin can also be added to the composition within such a range that the fire retardancy and mechanical properties of the composition will not be marred.

The fire retardant polyester resin composition according to the present invention is excellent in fire retardancy, mechanical properties and resistance to hydrolysis. In addition, the composition evolves no corrosive gases, so that it does not corrode a metal mold when it is molded. Moreover, the composition has a low specific gravity, and is excellent in flow characteristics. Therefore, the composition of the present invention can be suitably used for producing molded products which are thin-walled or complicated in shape. The polyester resin composition of the present invention is thus suitable as a material used for producing electrical or electronic equipments and parts thereof.

EXAMPLES

The present invention will now be explained more specifically by referring to the following examples. However, the present invention is not limited by these examples in any way.

Throughout the examples, the unit "part(s)" means "part(s) by weight".

The polyester resin compositions obtained in the following Examples and Comparative Examples were evaluated in terms of the following properties.

1) Fire Retardancy

The UL (Underwriter's Laboratories Inc.) 94 standard vertical flame test was carried out, and the limiting oxygen index ("LOI": ASTM D-2863, JIS K7201) was also determined to evaluate the fire retardancy.

2) Crystallisation Temperature (Tc) of Polymer

Under nitrogen atmosphere, a sample (approximately 10mg) was heated to a temperature of 260°C at a heating rate of 16°C/min, kept at the temperature for 5 minutes, and then cooled to 30°C at a cooling rate of 16°C/min by using a DSC (TA-2000) manufactured by Du Pont Inc., whereby the freezing point of the polymer was determined.

3) Flexural Properties

A bending test was carried out in accordance with ASTM D-790, and the flexural modulus (kgf/cm²) and flexural strength (kgf/cm²) were measured.

4) Impact Resistance

In accordance with ASTM D-256, a notched Izod impact test (abbreviated to "IZOD", unit kg-cm/cm) was carried out by using a notched specimen having a thickness of 1/8 inches.

5) Resistance to Hydrolysis

After a specimen was exposed to water vapor at 120°C for 24 hours, the above-described tensile test was carried out, and the retention of the tensile strength was obtained by the following equation:

$$\text{Retention \%} = \left(\frac{\text{Tensile strength after the exposure to water vapor}}{\text{Tensile strength before the exposure to water vapor}} \right) \times 100$$

6) Plate-Out

The surface of the metal mold used was visually observed.

7) Release Properties

A lattice specimen of 100 mm x 100 mm was made by injection molding. The cylinder temperature was 270°C, the mold temperature was 80°C, and the cooling time was 10 seconds. The pressure acted upon the center of the molded product when it was released from the metal mold by the aid of an ejector pin assembly was measured by a pressure sensor attached to the ejector pin assembly.

8) Flow Characteristics

The melt viscosity was measured at 260°C by using a "Shimadzu Flow Tester CFT 500" (nozzle: 1 mm (diameter) x 10 mm).

In Examples 1 to 30 and Comparative Examples 1 to 17, the following materials were used:

(a) polybutylene terephthalate having an intrinsic viscosity of 0.85, manufactured by Mitsubishi Engineering-Plastics Corp. (trade name "Novadur", hereinafter referred to as "PBT");

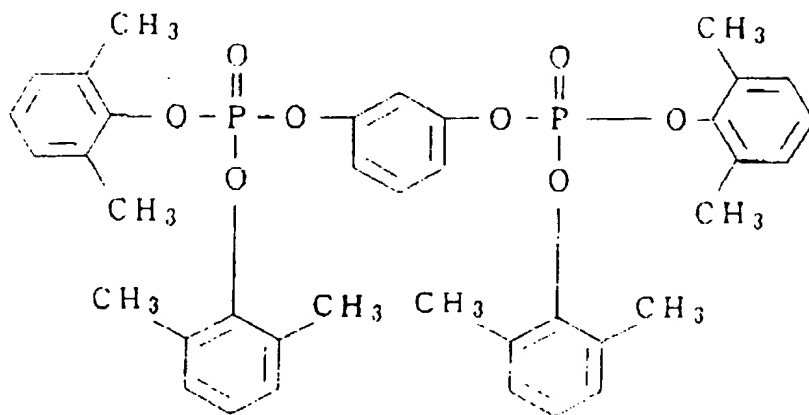
(b) PPE having an intrinsic viscosity of 0.45, manufactured by Mitsubishi Engineering-Plastics Corp. (trade name "Iupiac");

(c) bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite manufactured by Adeka Co., Ltd. (trade name "MARK PEP 36");

- (d) melamine cyanurate manufactured by Mitsubishi Engineering-Plastics Corp.;
- (e) glass fiber (3 mm chopped strand treated with epoxy silane) manufactured by Nippon Electric Glass Co., Ltd.;
- (f) milled fiber (a product treated with epoxy silane) manufactured by Nippon Electric Glass Co., Ltd.;
- (g) swelling synthetic mica manufactured by Co-op Chemical Co., Ltd. (trade name "ME 100");
- (h) organo-modified "ME 100" (example of modification: dimethyldistearyl ammonium);
- (i) epoxy-silane-treated "ME 100" ("ME 100" additioned with epoxy group);
- (j) epoxy-silane-treated organo-modified "ME 100" (organo-modified "ME 100" additioned with epoxy group);
- (k) polycarbonate having an intrinsic viscosity of 0.36, manufactured by Mitsubishi Engineering-Plastics Corp. (trade name "Novarex", hereinafter referred to as "PC");
- (l) liquid crystalline polyester manufactured by Mitsubishi Engineering-Plastics Corp. (trade name "Novacurate E 321", hereinafter referred to as "LCP");
- (m) polyethylene terephthalate having an intrinsic viscosity of 0.65, manufactured by Mitsubishi Chemical Corp. (trade name "Novapex", hereinafter referred to as "PET");
- (n) polystyrene having a melt flow index (at 200°C under a load of 5 kg) of 5.5 g/10 min, manufactured by Mitsubishi Chemical Corp. (trade name "Diarex", hereinafter referred to as "PSt");
- (o) polytetrafluoroethylene (ethylene tetrafluoride resin), manufactured by Daikin Industries, Ltd. (trade name "Polyfron F 201");
- (p) silicone oil having a high viscosity of 7,500 cs, manufactured by Shin-Etsu Silicone Co., Ltd. (trade name "KF-102");
- (q) "Modiper A 4100" manufactured by Nippon Oil & Fat Co., Ltd. (a comb-shaped polymer obtained by grafting polystyrene to ethylene-glycidyl methacrylate copolymer, abbreviated to "EGMA-g-PSt" (weight % ratio of EGMA/PSt = 70/30);
- (r) "Rezeda GP 500" manufactured by Toagosei Chemical Industry Co., Ltd. (a comb-shaped polymer obtained by grafting polystyrene to epoxy-modified polystyrene, abbreviated to "(Epo-PSt)-g-PSt"); and
- (s) epoxy-modified polystyrene (3.0 parts by weight of glycidyl methacrylate and 0.015 parts by weight of 2,5-dimethyl-2,5-di-(t-butylperoxy)hexane-3 were mixed with 100 parts by weight of polystyrene having a melt flow rate of 5.5 g/10 min, and the mixture was kneaded at a temperature of 210°C by using a twin-screw extruder having a diameter of 30 mm and then pelletized. After unreacted glycidyl methacrylate was acetone-extracted, the amount of the glycidyl methacrylate was determined from the ultraviolet absorption spectra. As a result, it was found that 1.7% by weight of the glycidyl methacrylate had been reacted).

Example 1

80 parts of the PBT, 20 parts of the PPE and 1.0 part of "MARK PEP 36" were blended. By using a bent-type twin-screw extruder ("Twin-Screw Extruder Labo TEX 30" manufactured by The Japan Steel Works, Ltd.) having a diameter of 30 mm, the mixture was melt-kneaded at a barrel temperature of 270°C, and extruded into strand. The strand was then pelletized by a strand cutter. The pellet thus obtained was dried, and then melt-kneaded with a dry blend consisting of, for 100 parts of the pellet, 15 parts of a phosphoric ester compound having the following structural formula (10):



... (10)

15 parts of the melamine cyanurate, 60 parts of the glass chopped strand and 2.0 parts of the epoxy-silane-treated "ME 100". The mixture was extruded into strand, and the strand was then pelletized by a strand cutter. The pellet obtained was molded into specimens by using an injection molding machine (type "J 28 SA" manufactured by The Japan Steel Works, Ltd.) and a metal mold for producing specimens for use in the UL 94 standard burning test or for producing specimens used for the determination of LOI (limiting oxygen index). The molding was carried out at a cylinder temperature of 270°C and a mold temperature of 80°C. By the use of the specimens, the evaluations were conducted.

Example 2

The procedure of Example 1 was repeated except that the amounts of the PET and the PPE were changed to 90 parts and 10 parts, respectively.

Example 3

The procedure of Example 1 was repeated except that the amounts of the PBT and the PPE were changed to 60 parts and 40 parts, respectively.

Example 4

The procedure of Example 1 was repeated except that the amounts of the PBT and the PPE were changed to 50 parts and 60 parts, respectively.

Example 5

The procedure of Example 4 was repeated except that the amount of the phosphoric ester compound having the structural formula (10) was changed to 30 parts and that the melamine cyanurate was not used.

Example 6

The procedure of Example 1 was repeated except that the amounts of the PBT and the PPE were changed to 40 parts and 60 parts, respectively.

Example 7

The procedure of Example 6 was repeated except that the amount of the glass chopped strand was changed to 65 parts and that the PSt was used in an amount of 10 parts.

Example 8

The procedure of Example 1 was repeated except that the glass chopped strand was not used.

Example 9

The procedure of Example 1 was repeated except that the amount of the glass chopped strand was changed to 20 parts.

Example 10

The procedure of Example 1 was repeated except that the amount of the glass chopped strand was changed to 100 parts.

Example 11

The procedure of Example 1 was repeated except that the amount of the milled fiber was changed to 60 parts.

Example 12

The procedure of Example 1 was repeated except that 2.0 parts of the organo-modified "ME 100" was used instead of 2.0 parts of the epoxy-silane-treated "ME 100".

Example 13

The procedure of Example 1 was repeated except that 2.0 parts of the epoxy-silane-treated organo-modified "ME 100" was used instead of 2.0 parts of the epoxy-silane-treated "ME 100".

Example 14

The procedure of Example 1 was repeated except that the amounts of the phosphoric ester compound having the structural formula (10) and the melamine cyanurate were changed to 7.5 parts and 22.5 parts, respectively.

Example 15

The procedure of Example 3 was repeated except that the amounts of the phosphoric ester compound having the structural formula (10) and the melamine cyanurate were changed to 22.5 parts and 7.5 parts, respectively.

Example 16

The procedure of Example 1 was repeated except that the amounts of the phosphoric ester compound having the structural formula (10) and the melamine cyanurate were changed to 10 parts and 10 parts, respectively.

Example 17

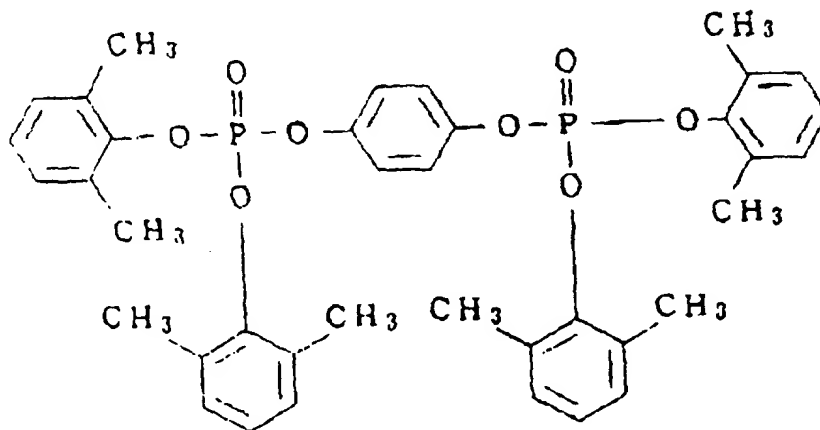
The procedure of Example 1 was repeated except that 0.05 parts of the polytetrafluoroethylene was used instead of 2.0 parts of the epoxy-silane-treated "ME 100".

Example 18

The procedure of Example 1 was repeated except that 1.0 part of the silicone oil was use instead of 2.0 parts of the epoxy-silane-treated "ME 100".

Example 19

The procedure of Example 1 was repeated except that 15 parts of a phosphoric ester compound having the following structural formula (11):

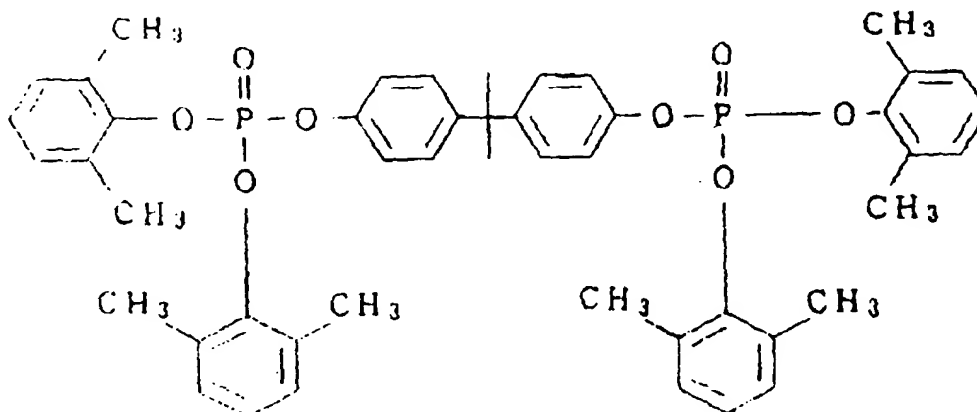


... (11)

was used instead of 15 parts of the phosphoric ester compound having the structural formula (10).

Example 20

The procedure of Example 1 was repeated except that 15 parts of a phosphoric ester compound having the following structural formula (12):

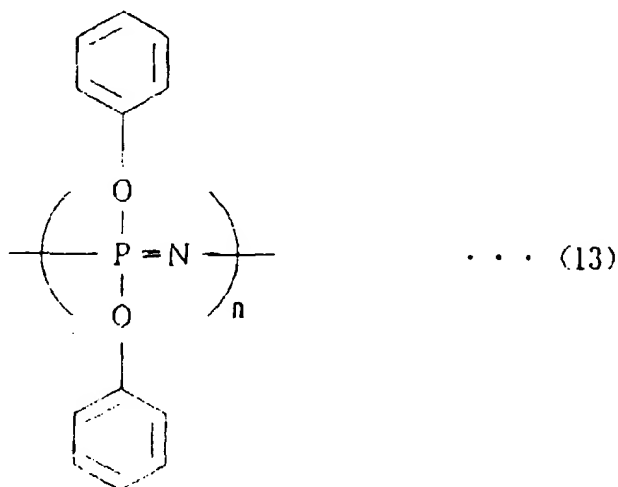


... (12)

was used instead of 15 parts of the phosphoric ester compound having the structural formula (10).

Example 21

The procedure of Example 1 was repeated except that 30 parts of a phosphonitrile compound having the following structural formula (13):



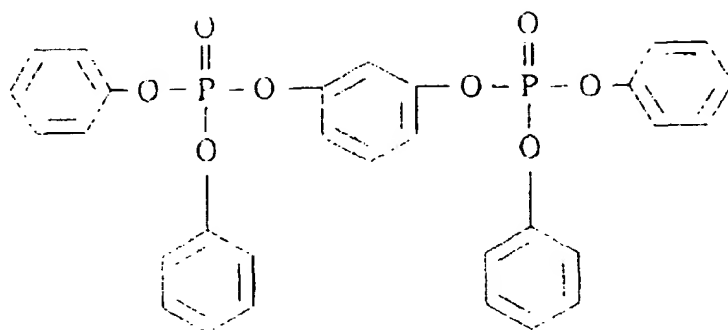
... (13)

wherein n is 3 or 4,

was used instead of 15 parts of the phosphoric ester compound having the structural formula (10) and 15 parts of the melamine cyanurate.

Example 22

The procedure of Example 1 was repeated except that 15 parts of a phosphoric ester compound having the following structural formula (14):



... (14)

was used instead of 15 parts of the phosphoric ester compound having the structural formula (10).

Example 23

The procedure of Example 1 was repeated except that 80 parts of the PET was used instead of 80 parts of the PBT.

Example 24

The procedure of Example 1 was repeated except that the amount of the PPE was changed to 15 parts and that the PPS was also used in an amount of 5.0 parts.

Example 25

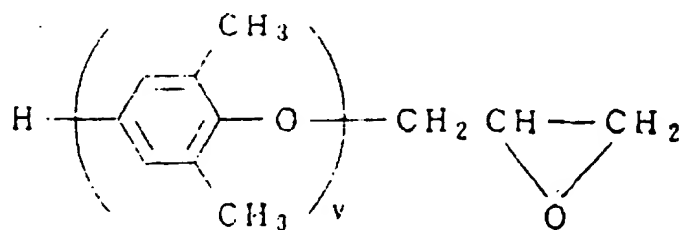
The procedure of Example 1 was repeated except that the amount of the PPE was changed to 5.0 parts and that the PPS was also used in an amount of 15 parts.

Example 26

The procedure of Example 1 was repeated except that 3.0 parts of xylene was added when the first kneading was conducted.

Example 27

The procedure of Example 1 was repeated except that 5.0 parts of an epoxy-group-added PPE having the following structural formula (15):



... (15)

was used instead of 1.0 part of the compatibilizing agent "MARK PEP 36" and that the amount of the PPE was changed to 15 parts.

Example 28

80 parts of the PBT, 20 parts of the PPE and 1.0 part of "MARK PEP 36" were blended. By using a bent-type twin-screw extruder ("Twin-Screw Extruder Labo TEX 30" manufactured by The Japan Steel Works, Ltd.) having a diameter of 30 mm, the mixture was melt-kneaded at a barrel temperature of 270°C, and extruded into strand. The strand was then pelletized by a strand cutter. The pellet thus obtained was dried, and then melt-kneaded with a dry blend consisting of for 100 parts of the pallet, 15 parts of a phosphoric ester compound having the above-described structural formula (10), 15 parts of the melamine cyanurate, 60 parts of the glass chopped strand, 2.0 parts of the epoxy-silane-treated "ME 100", and 4.0 parts of "Modiper A 4100". The mixture was extruded into strand, and the strand was then pelletized by a strand cutter. The pellet obtained was molded into specimens by using an injection molding machine (type "J 28 SA" manufactured by The Japan Steel Works, Ltd.) and a metal mold for producing specimens for use in the UL 94 standard burning test or for producing specimens used for the determination of LOI (limiting oxygen index) or for producing specimens for use in the ASTM test. The molding was carried out at a cylinder temperature of 270°C and a mold temperature of 80°C. By the use of the specimens, the evaluations were conducted.

Example 29

The procedure of Example 28 was repeated except that 4.0 parts of "Rezeda GP 500" was used instead of 4.0 parts of "Modiper A 4100".

Example 30

The procedure of Example 28 was repeated except that 4.0 parts of the epoxy-modified polystyrene (s) was used instead of 4.0 parts of "Modiper A 4100".

Comparative Example 1

The procedure of Example 1 was repeated except that the amount of the PBT was changed to 100 parts and that the PPE was not used. The composition remarkably deteriorated in fire retardancy and resistance to hydrolysis.

Comparative Example 2

The procedure of Example 1 was repeated except that the "MARK PEP 36" was not used. The composition remarkably deteriorated in fire retardancy, mechanical properties and resistance to hydrolysis.

Comparative Example 3

The procedure of Example 1 was repeated except that the amounts of the PBT and the PPE were changed to 60 parts and 40 parts, respectively, and that the "MARK PEP 36" was not used. The composition considerably deteriorated in fire retardancy, mechanical properties and resistance to hydrolysis.

Comparative Example 4

The procedure of Example 1 was repeated except that the amounts of the PET and the PPE were changed to 98 parts and 2.0 parts, respectively. The composition remarkably deteriorated in fire retardancy and resistance to hydrolysis.

Comparative Example 5

The procedure of Example 1 was repeated except that the amounts of the PBT and the PPE were changed to 10 parts and 90 parts, respectively. The resulting composition had a greatly increased melt viscosity.

Comparative Example 6

The procedure of Example 1 was repeated except that the amount of the phosphoric ester compound having the

structural formula (10) was changed to 30 parts and that the melamine cyanurate was not used. The composition deteriorated in fire retardancy and mechanical properties.

Comparative Example 7

The procedure of Example 1 was repeated except that the phosphoric ester compound having the structural formula (10) was not used and that the amount of the melamine cyanurate was changed to 30 parts. The composition considerably deteriorated in fire retardancy.

Comparative Example 8

The procedure of Example 1 was repeated except that the amounts of the phosphoric ester compound having the structural formula (10), the melamine cyanurate and the glass chopped strand were changed to 60 parts, 60 parts and 90 parts, respectively. The composition considerably deteriorated in resistance to hydrolysis, and showed greatly increased resistance to mold release. In addition, plate-out was also observed.

Comparative Example 9

The procedure of Example 1 was repeated except that the amounts of the phosphoric ester compound having the structural formula (10), the melamine cyanurate and the glass chopped strand were changed to 1.0 part, 1.0 part and 50 parts, respectively. The composition remarkably deteriorated in fire retardancy.

Comparative Example 10

The procedure of Example 1 was repeated except that the amount of the glass chopped strand was changed to 180 parts. The resulting composition had an extremely increased melt viscosity, and showed greatly increased resistance to mold release.

Comparative Example 11

The procedure of Example 1 was repeated except that the epoxy-silane-treated "ME 100" was not used. While the resulting composition was burning, the dripping of the resin was observed. The composition was thus found to be poor in fire retardancy.

Comparative Example 12

The procedure of Example 1 was repeated except that the amount of the epoxy-silane-treated "ME 100" was changed to 20 parts. The resulting composition had an extremely increased melt viscosity, showed greatly increased resistance to mold release, and was poor in mechanical properties.

Comparative Example 13

The procedure of Example 1 was repeated except that the amount of the "MARK PEP 36" was changed to 20 parts. The resulting composition showed greatly increased resistance to mold release, and was poor in mechanical properties. In addition, plate-out was also observed.

Comparative Example 14

The procedure of Example 1 was repeated except that the amount of the PBT was changed to 50 parts and that 50 parts of the LCP was used instead of 20 parts of the PPE. The resulting composition showed greatly increased resistance to mold release, and was very poor in resistance to hydrolysis and fire retardancy.

Comparative Example 15

The procedure of Example 1 was repeated except that the amount of the PBT as changed to 50 parts and that 50 parts of the polycarbonate was used instead of 20 parts of the PPE. The resulting composition showed greatly increased resistance to mold release, and was very poor in resistance to hydrolysis and fire retardancy.

Comparative Example 16

The procedure of Example 28 was repeated except that the amount of "MODIPER A 4100" was changed to 25 parts.

5 Comparative Example 17

The procedure of Example 30 was repeated except that the amount of the epoxy-modified polystyrene (s) was changed to 25 parts.

10 The formulations of the compositions of Examples 1 to 30 and Comparative Examples 1 to 17 are shown in Tables 1 to 6, and the results of the evaluations are shown in Tables 7 to 15.

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Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11
PBC (parts)	80	90	60	50	50	40	40	80	80	80	80
PPE (parts)	20	10	40	50	50	60	60	20	20	20	20
PEP36 (parts)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Phosphoric ester of formula (10) (parts)	15	15	15	15	30	15	15	15	15	15	15
Melamine cyanurate (parts)	15	15	15	15	-	15	15	15	15	15	15
Glass chopped strand (parts)	60	60	60	60	60	60	65	0	20	100	-
Milled fiber (parts)	-	-	-	-	-	-	-	-	-	-	60
Epoxy-silane-treated ME100 (parts)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
PSt (parts)	-	-	-	-	-	-	10	-	-	-	-

Table 2

	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20
	80	80	80	80	80	80	80	80	80
PI51 (parts)	20	20	20	20	20	20	20	20	20
PI4 (parts)	10	10	10	10	10	10	10	10	10
PI36 (parts)	15	15	7.5	22.5	10	15	15	-	-
Phosphoric ester of formula (10) (parts)								15	-
Phosphoric ester of formula (11) (parts)								-	15
Phosphoric ester of formula (12) (parts)								-	15
Melamine cyanurate (parts)	15	15	22.5	7.5	10	15	15	15	15
Glass chopped strand (parts)	60	60	60	60	60	60	60	60	60
Epoxy-silane-treated ME100 (parts)	-	-	2.0	2.0	2.0	-	-	2.0	2.0
Organo-modified ME100 (parts)	2.0	-	-	-	-	-	-	-	-
Epoxy-silane-treated organo-modified ME100 (parts)	-	2.0	-	-	-	-	-	-	-
Polytetrafluoroethylene (parts)	-	-	-	-	-	0.05	-	-	-
Silicone oil (parts)	-	-	-	-	-	-	1.0	-	-

Table 3

	Example 21	Example 22	Example 23	Example 24	Example 25	Example 26	Example 27
FBT (parts)	80	80	-	80	80	80	80
PET (parts)	-	-	80	-	-	-	-
PPA (parts)	20	20	20	15	50	20	15
PPS (parts)	-	-	-	50	15	-	-
PEP36 (parts)	10	10	10	10	10	10	-
Epoxy-group-added PPE (parts)	-	-	-	-	-	-	50
Phosphoric ester of formula (10) (parts)	-	-	15	15	15	15	15
Phosphonitrile having formula (13) (parts)	30	-	-	-	-	-	-
Phosphoric ester of formula (14) (parts)	-	15	-	-	-	-	-
Melamine cyanurate (parts)	-	15	15	15	15	15	15
Glass chopped strand (parts)	60	60	60	60	60	60	60
Epoxy-silane-treated ME100 (parts)	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Xylene (parts)	-	-	-	-	-	3.0	-

Table 4

	Example 28	Example 29	Example 30
FBT (parts)	80	80	80
FPE (parts)	20	20	20
PEP30 (parts)	10	10	10
Phosphoric ester of formula (10) (parts)	15	15	15
Melamine cyanurate (parts)	15	15	15
Glass chopped strand (parts)	60	60	60
Epoxy-silane-treated ME100 (parts)	2.0	2.0	2.0
MODIPER A 4100 (parts)	4.0	-	-
RESEDA CP 500 (parts)	-	4.0	-
Epoxy-modified P34 (parts)	-	-	4.0

Table 5

	Com- parative Example 1	Com- parative Example 2	Com- parative Example 3	Com- parative Example 4	Com- parative Example 5	Com- parative Example 6	Com- parative Example 7	Com- parative Example 8	Com- parative Example 9
PBT (parts)	100	80	60	98	10	80	80	80	80
PPE (parts)	-	20	40	2.0	90	20	20	20	20
PEP36 (parts)	1.0	-	-	1.0	1.0	1.0	1.0	1.0	1.0
Phosphoric ester of formula (10) (parts)	15	15	15	15	15	30	0	60	1.0
Melamine cyanurate (parts)	15	15	15	15	15	0	30	60	1.0
Glass chopped strand (parts)	60	60	60	60	60	60	60	90	50
Epoxy-silane-treated ME100 (parts)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

Table 6

	Com- parative Example 10	Com- parative Example 11	Com- parative Example 12	Com- parative Example 13	Com- parative Example 14	Com- parative Example 15	Com- parative Example 16	Com- parative Example 17
PBT (parts)	50	80	80	80	50	50	80	80
PPE (parts)	20	20	20	20	-	-	20	20
PCP (parts)	-	-	-	-	50	-	-	-
PCR (parts)	-	-	-	-	-	50	-	-
PEP56 (parts)	10	10	10	20	10	10	10	10
Phosphoric ester of formula (10) (parts)	15	15	15	15	15	15	15	15
Melamine cyanurate (parts)	15	15	15	15	15	15	15	15
Glass chopped strand (parts)	180	60	60	60	60	60	60	60
Epoxy-silane-treated ME100 (parts)	20	0	20	20	20	20	20	20
MODIPER A 4100 (parts)	-	-	-	-	-	-	25	-
Epoxy-modified polystyrene (parts)	-	-	-	-	-	-	-	25

Table 7

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Ul-94	V-0	V-0	V-0	V-0	V-0	V-0
LOI	31.5	29.8	32.4	33.4	32.9	34.6
Flexural modulus (kgf/cm ²)	79700	80600	77400	74800	75900	73100
Flexural strength (kgf/cm ²)	1940	1950	1910	1860	1880	1810
Retention of the tensile strength after exposure to water vapor (%)	86	82	89	84	81	86
T _g (°C)	201	201	198	194	188	192
Plate-out	not observed	not observed	not observed	not observed	not observed	not observed
Melt viscosity (poises)	3400	3200	4300	5600	4200	7700
Resistance to mold release (kgf/cm ²)	47	45	52	51	58	53
IZOD Impact strength (kg•cm/cm)	8.1	8.3	-	-	-	-

Table 8

	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
UL94	V-0	V-0	V-0	V-0	V-0	V-0
LOI	30.1	28.6	29.5	31.8	30.3	31.3
Tensile modulus (kgf/cm ²)	72500	27200	48800	122000	50100	79200
Flexural strength (kgf/cm ²)	1730	880	1470	2070	1260	1900
Retention of the tensile strength after exposure to water vapor (%)	84	80	86	90	77	85
T _g (°C)	180	200	202	202	201	200
Plate-out	not observed	not observed	not observed	not observed	not observed	not observed
Melt viscosity (poises)	5900	2300	2800	5200	2900	3300
Resistance to mold release (kgf/cm ²)	56	49	49	47	48	47
IZOD Impact strength (kg·cm/cm)	-	-	-	-	-	-

Table 9

	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
UL94	V-0	V-0	V-0	V-0	V-0	V-0
ICI	521	313	316	301	310	309
Flexural modulus (kgf/cm ²)	80200	79500	78900	79900	79000	78800
Flexural strength (kgf/cm ²)	2660	1930	1840	1950	1960	1870
Retention of the tensile strength after exposure to water vapor (%)	85	88	79	89	84	85
T _g (°C)	200	202	198	201	202	197
Plate-out	not observed	not observed	not observed	not observed	not observed	not observed
Melt viscosity (poises)	3500	3500	2900	3700	4200	4400
Resistance to mold release (kgf/cm ²)	48	46	45	48	54	58
IZOD Impact strength (kg•cm/cm)	-	-	-	-	-	-

Table 10

	Example 19	Example 20	Example 21	Example 22	Example 23	Example 24
UV 94	V-0	V-0	V-0	V-0	V-0	V-0
LCI	31.3	30.5	30.8	30.4	31.9	31.9
Flexural modulus (kgf/cm ²)	79500	79100	79000	79900	78700	80200
Flexural strength (kgf/cm ²)	1940	1910	1920	1950	1900	1940
Retention of the tensile strength after exposure to water vapor (%)	84	82	93	58	85	84
T _c (°C)	200	202	200	202	200	200
Plate-out	not observed	not observed	not observed	not observed	not observed	not observed
Melt viscosity (poises)	3500	3600	3500	3500	3200	3800
Resistance to mold release (kgf/cm ²)	48	49	49	47	45	49
IZOD impact strength (kg·cm/cm)	-	-	-	-	-	-

Table II

	Example 25	Example 26	Example 27
UV-94	V-0	V-0	V-0
LOI	32.2	31.6	30.2
Flexural modulus (kg/cm ²)	81500	80700	76700
Flexural strength (kg/cm ²)	1950	2030	1830
Retention of the tensile strength after exposure to water vapour (%)	85	87	83
T _g (°C)	201	201	198
Plate-out	not observed	not observed	not observed
Melt viscosity (poises)	4400	3400	3700
Resistance to mold release (kg/cm ²)	48	46	57
IZOD Impact strength (kg·cm/cm)	-	-	-

Table 12

	Example 28	Example 29	Example 30
UL 94	V-0	V-0	V-0
LOI	30.9	30.4	30.8
Flexural modulus (kgf/cm ²)	80900	80600	81000
Flexural strength (kgf/cm ²)	1970	1950	1960
Retention of the tensile strength after exposure to water vapor (%)	90	87	89
T _g (°C)	201	199	200
Plate-out	not observed	not observed	not observed
Melt viscosity (poises)	3400	3500	3400
Resistance to mold release (kgf/cm ²)	48	54	51
IZOD Impact strength (kg·cm/cm)	10.5	10.2	10.4

Table 15

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
1.1.24	V-2	V-2	V-2	V-2	V-2	V-2
1.01	23.2	26.1	27.9	23.4	34.7	25.9
Flexural modulus (kgf/cm ²)	7550	65200	70400	79700	62400	72100
Flexural strength (kgf/cm ²)	1940	990	1030	1890	1570	1020
Retention of the tensile strength after exposure to water vapor (%)	31	25	29	14	88	85
T _g (°C)	202	199	200	201	168	171
Plate-out	not observed	not observed	not observed	not observed	not observed	not observed
Melt viscosity (poises)	3100	3800	4800	3100	14300	3400
Resistance to mold release (kgf/cm ²)	46	47	52	47	184	152
IZOD Impact strength (kg·cm/cm)	6.2	2.3	2.1	6.4	-	-

Table 14

	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10	Comparative Example 11	Comparative Example 12
III 94	V-2	V-0	V-2	V-0	V-2	V-2
LOI	25.6	32.0	25.7	29.7	26.1	23.7
Flexural modulus (kgf/cm ²)	73400	75700	78300	133000	78700	65100
Flexural strength (kgf/cm ²)	1860	1020	1850	1570	1880	1070
Retention of the tensile strength after exposure to water vapor (%)	81	14	87	83	84	62
T _g (°C)	201	192	201	200	200	182
Plate-out	not observed	observed	not observed	not observed	not observed	observed
Melt viscosity (poises)	13900	2800	4100	9100	3600	8200
Resistance to mold release (kgf/cm ²)	44	143	49	141	46	153
IZOD Impact strength (kg•cm/cm)	-	-	-	-

Table 15

	Example 13	Example 14	Example 15	Example 16	Example 17
EH 94	V-2	V-2	V-2	V-2	V-2
LOI	23.9	26.3	25.5	26.1	26.3
Flexural modulus (kgf/cm ²)	66400	73200	75300	68200	66100
Flexural strength (kgf/cm ²)	1270	1810	1780	1620	1640
Retention of the tensile strength after exposure to water vapor (%)	34	28	25	85	81
T _g (°C)	172	171	173	199	198
Plate-out	observed	not observed	not observed	not observed	not observed
Melt viscosity (poises)	4200	3500	4100	3900	3700
Resistance to mold release (kgf/cm ²)	173	158	154	168	181
IZOD Impact strength (kg·cm/cm)	..	-	-	5.7	5.3

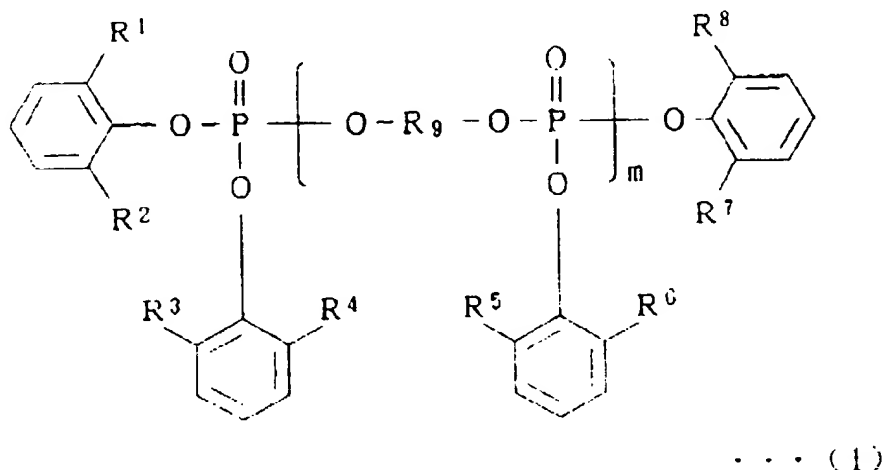
Claims

1. A fire retardant polyester resin composition comprising the following components (A) to (H):

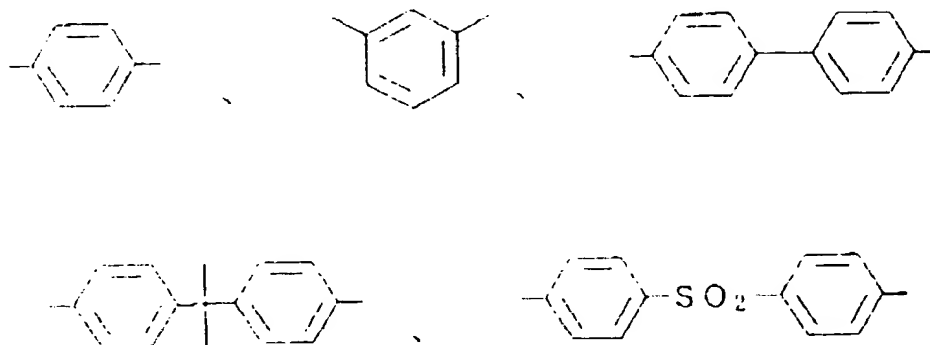
- (A) 95 to 30 parts by weight of a polyester resin, and
 (B) 5.0 to 70 parts by weight of a polyphenylene ether resin and/or polyphenylene sulfide resin, and, for 100 parts by weight in total of the components (A) and (B),
 (C) 0.05 to 10 parts by weight of a compatibilizing agent,
 (D) 2.0 to 45 parts by weight of a phosphoric ester compound or phosphonitrile compound,
 (E) 0 to 150 parts by weight of a reinforcing filler, (F) 0.001 to 15 parts by weight of an anti-dripping agent,
 (G) 0 to 45 parts by weight of a melamine cyanurate, and
 (H) 0 to 15 parts by weight of a polystyrene resin having epoxy group,
 provided that the amount of the component (G) is from 0.5 to 45 parts by weight for 100 parts by weight in total of the components (A) and (B) when the amount of the component (B) is less than 35 parts by weight.

2. The fire retardant polyester resin composition according to claim 1, wherein the compatibilizing agent, the component (C), is a phosphorous triester.

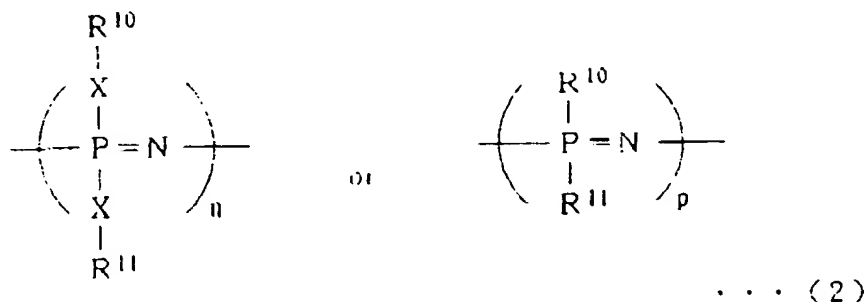
3. The fire retardant polyester resin composition according to claim 1 or 2, wherein the phosphoric ester compound or phosphonitrile compound, the component (D), is a phosphoric ester compound represented by the general formula (1):



wherein R¹ to R⁸ are hydrogen atom or an alkyl group having 1 to 6 carbon atoms, m is 0 or an integer of 1 to 4, and R⁹ represents a structure selected from the following:



4. The fire retardant polyester resin composition according to claim 1, wherein the phosphoric ester compound or phosphonitrile compound, the component (D), is a phosphonitrile compound having a group represented by the general formula (2):



wherein X represents O, S or N-H, R¹⁰ and R¹¹ are an aryl, alkyl or cycloalkyl group having 1 to 20 carbon atoms, -X-R¹⁰ and -X-R¹¹ may be the same or different, and n and p are an integer of 1 to 12.

5. The fire retardant polyester resin composition according to any of claims 1 to 4, comprising 0.1 to 15 parts by weight for 100 parts by weight in total of the components (A) and (B) of a layered silicate as the anti-dripping agent, the component (F).
6. The fire retardant polyester resin composition according to claim 5, wherein the layered silicate has a reactive functional group.
7. The fire retardant polyester resin composition according to any of claims 1 to 4, comprising 0.001 to 10 parts by weight for 100 parts by weight in total of the components (A) and (B) of a fluorine-containing polymer as the anti-dripping agent, the component (F).
8. The fire retardant polyester resin composition according to any of claims 1 to 4, comprising 0.001 to 10 parts by weight for 100 parts by weight in total of the components (A) and (B) of a silicone oil as the anti-dripping agent, the component (F).
9. The fire retardant polyester resin composition according to any of claims 1 to 8, wherein the polyphenylene ether resin and/or polyphenylene sulfide resin, the component (B), is a mixture of a polyphenylene ether resin and a polyphenylene sulfide resin in a weight % ratio of (5 - 99) : (95 - 1).
10. The fire retardant polyester resin composition according to any of claims 1 to 9, wherein the polyester resin, the component (A), is a polyalkylene terephthalate.
11. A process for producing a fire retardant polyester resin composition comprising the following components (A) to (H):
- (A) 95 to 30 parts by weight of a polyester resin, and
 - (B) 5.0 to 70 parts by weight of a polyphenylene ether resin and/or polyphenylene sulfide resin, and, for 100 parts by weight in total of the components (A) and (B),
 - (C) 0.05 to 10 parts by weight of a compatibilizing agent,
 - (D) 2.0 to 45 parts by weight of a phosphoric ester compound or phosphonitrile compound,
 - (E) 0 to 150 parts by weight of a reinforcing filler,
 - (F) 0.001 to 15 parts by weight of an anti-dripping agent,
 - (G) 0 to 45 parts by weight of a melamine cyanurate, and

(H) 0 to 15 parts by weight of a polystyrene resin having epoxy group,
provided that the amount of the component (G) is from 0.5 to 45 parts by weight for 100 parts by weight in
total of the components (A) and (B) when the amount of the component (B) is less than 35 parts by weight,
in which the polyester resin (the component (A)), the polyphenylene ether resin and/or polyphenylene sulfide
resin (the component (B)) and the compatibilizing agent (the component (C)) are firstly melt-kneaded to form
a mixture, and the mixture is then melt-kneaded with the other components (D) to (H) to obtain the desired
fire retardant polyester resin composition.

12. The process for producing the fire retardant polyester resin composition according to claim 11, wherein the poly-
ester resin (the component (A)), the polyphenylene ether resin and/or polyphenylene sulfide resin (the component
(B)), and the compatibilizing agent (the component (c)) are melt-kneaded under the presence of an organic solvent
in which the component (B) can be dissolved.

13. The process for producing the fire retardant polyester resin composition according to claim 11 or 12, wherein the
polyphenylene ether resin and/or polyphenylene sulfide resin, the component (B), is a mixture of a polyphenylene
ether resin and a polyphenylene sulfide resin in a weight % ratio of (5 - 99) : (95 - 1).

(19)



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(54) **Fire retardant polyester resin composition and process for producing the same**

(57) A fire retardant polyester resin composition comprising (A) 95 to 30 parts by weight of a polyester resin and (B) 5.0 to 70 parts by weight of a polyphenylene ether resin and/or polyphenylene sulfide resin, and, for 100 parts by weight in total of the components (A) and (B), (C) 0.05 to 10 parts by weight of a compatibilizing agent, (D) 2.0 to 45 parts by weight of a phosphoric ester compound or phosponitrile compound, (E) 0 to 150 parts by weight of a reinforcing filler, (F) 0.001

to 15 parts by weight of an anti-dripping agent, (G) 0 to 45 parts by weight of a melamine cyanurate, and (H) 0 to 15 parts by weight of a polystyrene resin having epoxy group, provided that the amount of the component (G) is from 0.5 to 45 parts by weight for 100 parts by weight in total of the components (A) and (B) when the amount of the component (B) is less than 35 parts by weight. The polyester resin composition scarcely corrodes a metal mold when it is molded, and is excellent in fire retardancy.

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EUROPEAN SEARCH REPORT

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EP 97 30 1216

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication where appropriate of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl. 6)
Y	EP 0 491 986 A (GENERAL ELECTRIC COMPANY) * page 2, line 1-25: claims 1-8 *	1-4.9-12	C08L67/02 C08K5/49 C08K5/00
Y	EP 0 593 054 A (MITSUBISHI PETROCHEMICAL CO., LTD.) * claims 1-12 *	1-4.9-12	C08K5/3492 /(C08L67/02, 71:02,81:04), (C08L67/02, 71:02), (C08L67/02, 81:04)
Y	PATENT ABSTRACTS OF JAPAN vol. 18, no. 528 (C-1258), 6 October 1994 & JP 06 184357 A (ASAHI CHEM IND CO LTD), 5 July 1994, * abstract *	1-4.9-12	
A	EP 0 133 641 A (GENERAL ELECTRIC COMPANY) * claims 1-29 *	1.3.4	
D	& JP 60 047 056 A (GENERAL ELECTRIC COMPANY) 14 March 1985		
A	DATABASE WPI Week 9429 Derwent Publications Ltd., London, GB: AN 94-238972 XP002047758 & JP 06 172 658 A (ASAHI KASEI KOGYO KK), 21 June 1994 * abstract *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08L C08K
A	US 3 365 783 A (CLUTTER) * claims 1-8 *	1.3.4	
A	EP 0 468 772 A (POLYPLASTICS CO., LTD) * claim 1 *	1	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		21 November 1997	Decocker, L
CATEGORY OF CITED DOCUMENTS		F : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons S : member of the same patent family, corresponding document	
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